



GB04/4255



INVESTOR IN PEOPLE

The Patent Office  
 Concept House  
 Cardiff Road  
 Newport  
 South Wales  
 NP10 8QQ

## PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN  
 COMPLIANCE WITH RULE 17.1(a) OR (b)

REC'D 03 DEC 2004

WIPO

PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated

24 November 2004



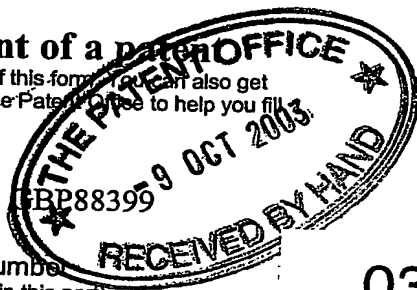
BEST AVAILABLE COPY

THIS PAGE BLANK (USPTO)

THIS PAGE BLANK (USPTO)

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

EBP88399

2. Patent application number  
(The Patent Office will fill in this part)

0323671.8

3. Full name, address and postcode of the or of each applicant (underline all surnames)

University of Southampton,  
Highfield  
Southampton SO17 1BJ  
United Kingdom

Patents ADP number (if you know it)

798470001

If the applicant is a corporate body, give the country/state of its incorporation

England

4. Title of the invention

VAPOUR DEPOSITION METHOD

5. Name of your agent (if you have one)  
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Marks & Clerk  
57 - 60 Lincolns Inn fields  
London WC2A 3LS

Patents ADP number (if you know it)

18001✓

6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months

Country

Priority application No  
(if you know it)

Date of filing  
(day / month / year)

7. Divisionals, etc: Complete this section only if this application is a divisional, application or resulted from an entitlement dispute

Number of earlier application

Date of filing  
(day / month / year)

8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request?

Yes

(Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See note (d))

# Patents Form 1/77

9. ☒ Accompanying documents: A patent application must include a description of the invention. Not counting duplicates, please enter the number of pages of each item accompanying this form:

Continuation sheets of this form 0

Description 8

Claim(s) 1

Abstract 1

Drawing(s) 3

10. If you are also filing any of the following, state how many against each item.

## Priority documents

Translations of priority documents /

Statement of inventorship and right to grant of a patent (Patents Form 7/77) 1 /

Request for preliminary examination and search (Patents Form 9/77) 1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature(s) Mark Seclark

Date: 9 October 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

Patent Chemical Formalities  
020 7400 3000

BEST AVAILABLE COPY

### VAPOUR DEPOSITION METHOD

5       The present invention relates to a novel vapour deposition method which can be used to deposit mixtures of materials in progressively varying amounts on a substrate and which can be used for a variety of purposes, but is of especial value in combinatorial chemistry.

10       The basis of combinatorial chemistry is to form large libraries of molecules in a single process step, instead of synthesizing compounds individually, as was hitherto traditional, and to identify the most promising compounds by high throughput screening of the compounds in the libraries. Although originally used mainly in the pharmaceutical industry, it has since found more widespread use throughout the chemical industries, and has been extended to the synthesis of inorganic materials. By  
15       application of the present invention, it is possible to apply the techniques of combinatorial chemistry to the preparation of metal alloys and inorganic materials by vapour deposition.

20       Combinatorial chemistry, as it applies to the present invention, requires the deposition of materials in relative amounts that vary progressively in at least one direction along a substrate. US6,045,671 discloses a method of achieving this in which a shadow mask or masks is or are moved directly in front of a substrate between a source (of the vapour deposited material) and the substrate, so as to expose positions on the substrate to increasing amounts of material in proportion to the time that these  
25       positions lie in direct line of sight of the source. Necessarily, such an arrangement can only be used with a single source at one time. Accordingly, if this process is to be used to produce a mixture of materials, as is necessary for combinatorial chemistry, the coated substrate has to be subjected to a second pass using a second source, and then the deposited material has to be mixed in some way without disturbing the relative concentrations of the materials at different positions on the substrate. According to

US6,045,671, this is done by heated the deposited materials. However, in practice, the effectiveness of heating as a method of mixing can be limited, and it cannot be used at all with heat-sensitive materials.

There is, therefore, a need in combinatorial chemistry for a method for the  
5 simultaneous deposition of two or more materials in uniformly varying amounts, the  
amounts varying according to a pre-arranged pattern according to location on the  
substrate.

We have now discovered that this may be achieved without using a moving  
mask, by careful positioning of a mask between source and target. A further benefit of  
10 the inventive method is that it can be used for other purposes than combinatorial  
chemistry where a progressively varying thickness of one or more materials on a  
substrate is required.

Thus, the present invention consists in a vapour deposition process, in which a  
material is vaporised from a source and deposited on a substrate, the path of the  
15 vaporised material from the source to the substrate being partially interrupted by a  
mask, the positioning of the mask in a plane parallel to the plane defined by the  
substrate being such that the material is deposited on the substrate in a thickness which  
increases substantially continuously in a direction along the substrate.

The source should be of finite size, i.e. it should not be a point source.

20 Where a plane is defined by the centres of the source and the substrate and  
intersecting an edge of the mask, the mask is so positioned that its intersection with that  
plane lies within the boundaries defined by the intersection of the surface of the source  
with the plane and the lines in that plane joining each edge of the source with the  
opposite edge of the substrate.

25 Preferably, the mask is positioned closer to the source than to the substrate, but  
in any case sufficiently far from the substrate to produce a range of deposition rates  
across the sample without movement of the mask during deposition. This contrasts  
strongly with the method of US6,045,671, where the mask is positioned immediately  
next to the substrate, and must be moved during deposition.

If desired, there may be two or more sources, as defined above, depositing material on a single substrate, each source being associated with a mask positioned as defined above and preferably closer to the source than to the substrate, the positioning of the mask in a plane parallel to the plane defined by the substrate being such that the material from each source is deposited on the substrate in a thickness which increases substantially continuously in a direction along the substrate.

In accordance with the present invention, where there is a single mask for a given source, the thickness of the deposited material will vary along one dimension of the substrate. However, if desired, by providing a second mask, suitably located, the thickness may be caused to vary along two dimensions of the substrate.

Although the mask does not move in the course of the process of the present invention, it is preferably movable so that, with the use of different sources and/or substrates, it can be moved into the appropriate position to produce the required gradient.

The mask may be of any suitable shape, provided that it can "hide" a part of the source from the substrate. It may be an aperture in a cover located between the source and the substrate. Where there are several sources and correspondingly several masks, this may be the most convenient option.

The source, substrate, vapour deposited material and vapour deposition apparatus are all conventional and are well known to those skilled in the art, and so will not be described in detail herein. Suitable apparatus are typically designed for the deposition of compound semi-conductors, of metals on silicon substrates, in semiconductor fabrication.

The process of the present invention may be applied to many materials, examples of which include: metal alloys (binary, ternary, quaternary etc.) mixed oxides, doped oxides, mixed nitrides etc.

The process will normally take place in a vacuum chamber, as is conventional. Where there are several sources and a single substrate, the sources are preferably arranged approximately equidistant from the axis through the centre of the substrate.

The method may also be applied to a source positioned along the centre axis normal to the substrate. As few as 1 or 2 and as many as 6 or 8 sources can be used at the same time.

The invention is further illustrated by the accompanying drawings, in which:

5 Figure 1 shows a schematic diagram of a three source physical vapour deposition system for the simultaneous deposition of materials onto a substrate;

Figure 2 shows in more detail a schematic diagram of one of the off-centre sources of Figure 1; and

10 Figure 3 shows a plot of thickness against position of two samples prepared using a single source, as described in more detail hereafter.

The provision of the masks allows a graded ("wedge") deposition of each of the materials across the sample. The characteristic gradient of the wedge growth is determined by the position of the mask with respect to the sample and the source. By using the wedge growth method on several sources simultaneously allows the  
15 deposition of a thin film of variable composition as a function of position across the sample. Although in plane deposition is depicted in Figure 1, sources may be combined out of plane and mixed compositions of a large number of elements are achievable. This methodology is ideal for high-throughput or combinatorial methodologies of materials growth.

20 In order to establish the conditions required for optimal wedge growth, deposition has been simulated for a number of geometries. Simulations have been carried out for a source of providing constant flux across its face, and this can be modified to include variations across the face of the source in the cases of, for example, locally heated e-beam sources. The simulation is carried out in two dimensions, since  
25 this provides sufficient detail to in a first approximation to predict the wedge growth.

~~Figure 2 shows the detailed geometric arrangement, defined lengths and positions of a~~  
typical "off axis" source. Note that similar effects are achievable with an on axis source. Note that the origin to which distances are referenced (0,0) is defined as the centre of the sample face.



A Sample size

$A_1$  and  $A_2$  The points of the extremities of the sample.

B Offset of mask with respect to the axis centre of the source. The mask is shown in the position  $B_{\min}$ .

5 C Source size (as defined by the finite region from which the source material emanates).

$C_1$  and  $C_2$  The points of the extremities of the source.

D Offset of source with respect to the sample.

E Source to mask distance

10 F Mask to sample distance

Four points of interest can be defined for the position of the mask in x with respect to the projected flux of the source. They correspond to the intersection of the mask with the line of sight of the extremities of the source and sample (lines  $A_1, C_1, A_2, C_2$ ). Those four points have been defined as  $B_{\min}$ ,  $B_1$ ,  $B_2$  and  $B_{\max}$ . The position of the mask corresponding to these positions can be calculated geometrically.

$B_{\min}$  is defined as the point at which the mask cuts the line  $A_2C_2$ , and its position in x with respect to the centre of the source is given by:

$$B_{\min} = \frac{1}{2} \left[ \frac{(A - 2D)E + CF}{(E + F)} \right]$$

$B_{\max}$  is defined as the point at which the mask cuts the line  $A_1C_1$ , and its position in x with respect to the centre of the source is given by:

$$B_{\max} = -\frac{1}{2} \left[ \frac{(A + 2D)E + CF}{(E + F)} \right]$$

$B_1$  is defined as the point at which the mask cuts the line  $A_1C_2$ , and its position in x with respect to the centre of the source is given by:

$$B_1 = -\frac{1}{2} \left[ \frac{(A+2D)E - CF}{(E+F)} \right]$$

$B_2$  is defined as the point at which the mask cuts the line  $A_2C_1$ , and its position in  $x$  with respect to the centre of the source is given by:

$$B_2 = -\frac{1}{2} \left[ \frac{(2D-A)E + CF}{(E+F)} \right]$$

- 5 A further point of interest can be identified and is labelled  $H$ , and is defined as the intersection of the two source flux lines  $A_1C_2$  and  $A_2C_1$ . The coordinates of point  $H$  ( $H_x, H_y$ ) with respect to the point of origin (the point of origin being the centre of the sample face 0,0) are given by:

$$H_x = \frac{AD}{A+C}$$

10 
$$H_y = \frac{(E+F)A}{A+C}$$

- Wedge growth of various qualities is achieved by using a mask that cuts the direct path between the source and the substrate, i.e. the quadrilateral defined by  $A_1, A_2, C_2, C_1$  in 2D projection. Simulations show that the triangle defined by  $H, C_1$  and  $C_2$  gives the region in which the mask cutting the source flux will give rise to linear gradients across the entire sample. For an mask which cuts the flux in all other positions, incomplete or no wedge growth is obtained. In summary:
- 15

For  $F > H_y$ ,  $B_{\min} > B_1 > B_2 > B_{\max}$ . If:

$B > B_{\min}$  Uniform film (natural profile of unimpeded source)

$B_{\min} > B > B_1$  Partial gradient across sample (plateau + gradient)

20  $B_1 > B > B_2$  Linear gradient across whole sample

$B_2 > B > B_{\max}$  Partial gradient across sample (gradient + no deposition)

$B_{\max} > B$  No deposition

For  $F < H_y$ ,  $B_{\min} > B_2 > B_1 > B_{\max}$  If:

$B > B_{\min}$  Uniform film (natural profile of unimpeded source)

$B_{\min} > B > B_2$  Partial gradient across sample (plateau + gradient)

5  $B_2 > B > B_1$  Partial gradient across sample (plateau + gradient + no deposition)

$B_1 > B > B_{\max}$  Partial gradient across sample (gradient + no deposition)

$B_{\max} > B$  No deposition

10 Hence, in accordance with the present invention, provided the mask is correctly positioned at first, and this can easily be achieved by following the above guidance, a gradient distribution of material is obtained without moving the mask in the course of the process.

15 Table 1 shows the results of a simulation for a specific growth geometry, calculating the expected deposition profiles for the mask moving across the full range of the source flux to the sample. The fixed values (in mm) used were  $A = 22$ ,  $C = 20$ ,  $D = 162$ ,  $E = 150$  and  $F = 350$ . This gives  $B_{\min} = -38.3$ ,  $B_1 = -44.9$ ,  $B_2 = -52.3$  and  $B_{\max} = -58.9$ .

20 "Maximum Flux" is defined as the maximum percentage of source material deposited on the sample with respect to the amount of material that would have been deposited had no mask been used.

"Minimum Flux" is defined as the minimum percentage of material deposited on the sample with respect to the amount of material that would have been deposited had no mask been used.

25 The "Normalised Gradient" corresponds to the percentage difference between the maximum and minimum amounts deposited across the sample. Note that the

deposition (the way this Normalised Gradient is deposited) does not always take place in a continuous gradient (labelled linear gradient) across the sample.

Table 1

<i>B / mm</i>	<i>Max Flux</i> <i>/-%</i>	<i>Min Flux</i> <i>/-%</i>	<i>Normalised</i> <i>Gradient- /</i> <i>%</i>	<i>Predicted</i> <i>Profile</i>
-59	0	0	0-0	No deposit
-58	5.86	0	0-100	No deposit + gradient
-57	12.69	0	0-100	No deposit + gradient
-56	19.51	0	0-100	No deposit + gradient
-55	26.32	0	0-100	No deposit + gradient
-54	34.08	0	0-100	No deposit + gradient
-53	40.86	0	0-100	Linear gradient
-52	47.63	4.00	8.4-100	Linear gradient
-51	54.39	11.00	20.22-100	Linear gradient
-50	61.13	17.98	29.42-100	Linear gradient
-49	67.87	24.96	36.77-100	Linear gradient
-48	74.59	31.92	42.80-100	Linear gradient
-47	82.26	38.87	47.26-100	Linear gradient
-46	88.96	45.82	51.51-100	Linear gradient
-45	95.64	53.74	56.19-100	Linear gradient
-44	97.77	60.66	62.05-100	Linear gradient
-43	98.18	67.57	68.82-100	Plateau + gradient
-42	98.59	74.47	75.53-100	Plateau + gradient
-41	99.00	81.3	82.18-100	Plateau + gradient
-40	99.41	88.24	88.76-100	Plateau + gradient
-39	99.70	95.10	95.38-100	Plateau + gradient
-38	100.00	97.55	97.55-100	Natural profile of source

5

Figure 3 shows the results of simulations, and corresponding experimental data, for the deposition of gold on a SiN substrate. The source was a Knudsen cell with dimension C = 20 mm, A = 26 mm, E = 350 mm, F = 150 mm and D = 162 mm. B was varied for the 2 examples between B = -51.8 mm for sample 9 and B = -45 mm for sample 12.

10

**CLAIMS:**

1. A vapour deposition process, in which a material is vaporised from a source and deposited on a substrate, the path of the vaporised material from the source to the substrate being partially interrupted by a mask, the positioning of the mask in a plane parallel to the plane defined by the substrate being such that the material is deposited on the substrate in a thickness which increases substantially continuously in a direction along the substrate.
2. A process according to Claim 1, where a plane is defined by the centres of the source and the substrate and intersecting an edge of the mask, and the mask is so positioned that its intersection with that plane lies within the boundaries defined by the intersection of the surface of the source with the plane and the lines in that plane joining each edge of the source with the opposite edge of the substrate.
3. A process according to Claim 1 or Claim 2, where the mask is positioned closer to the source than to the substrate.
4. A process according to any one of Claims 1 to 3, where there are two or more sources depositing material simultaneously on a single substrate, each source being associated with a mask positioned as defined in Claim 1.

**ABSTRACT:****Vapour Deposition Method**

In a vapour deposition method which can be used to deposit mixtures of materials in progressively varying amounts on a substrate and which can be used for a variety of purposes, but is of especial value in combinatorial chemistry, the path of the vaporised material from the source to the substrate is partially interrupted by a mask, the positioning of the mask in a plane parallel to the plane defined by the substrate being such that the material is deposited on the substrate in a thickness which increases substantially continuously in a direction along the substrate.

BEST AVAILABLE COPY

Figure 1

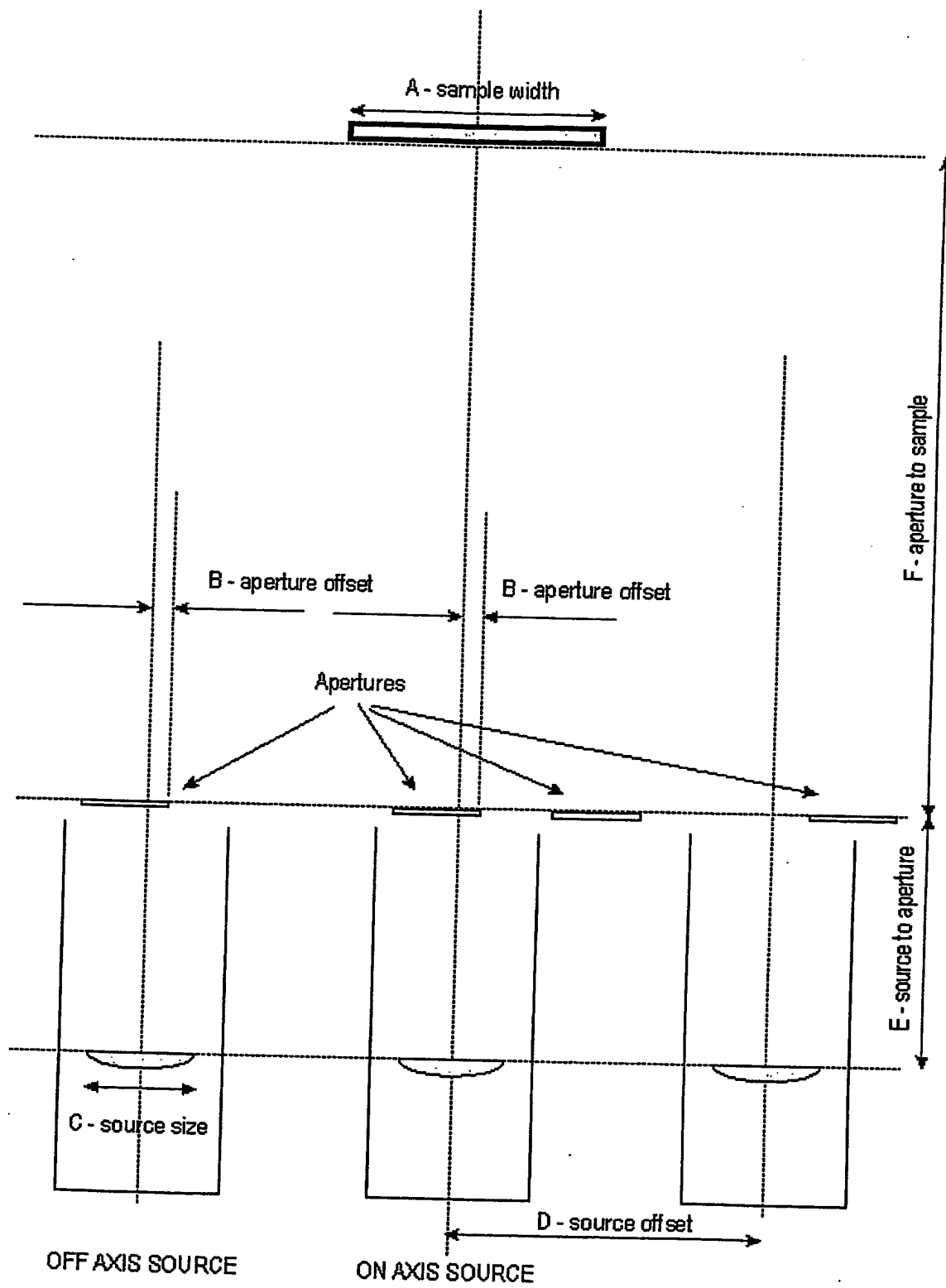


Figure 2  
D - source offset

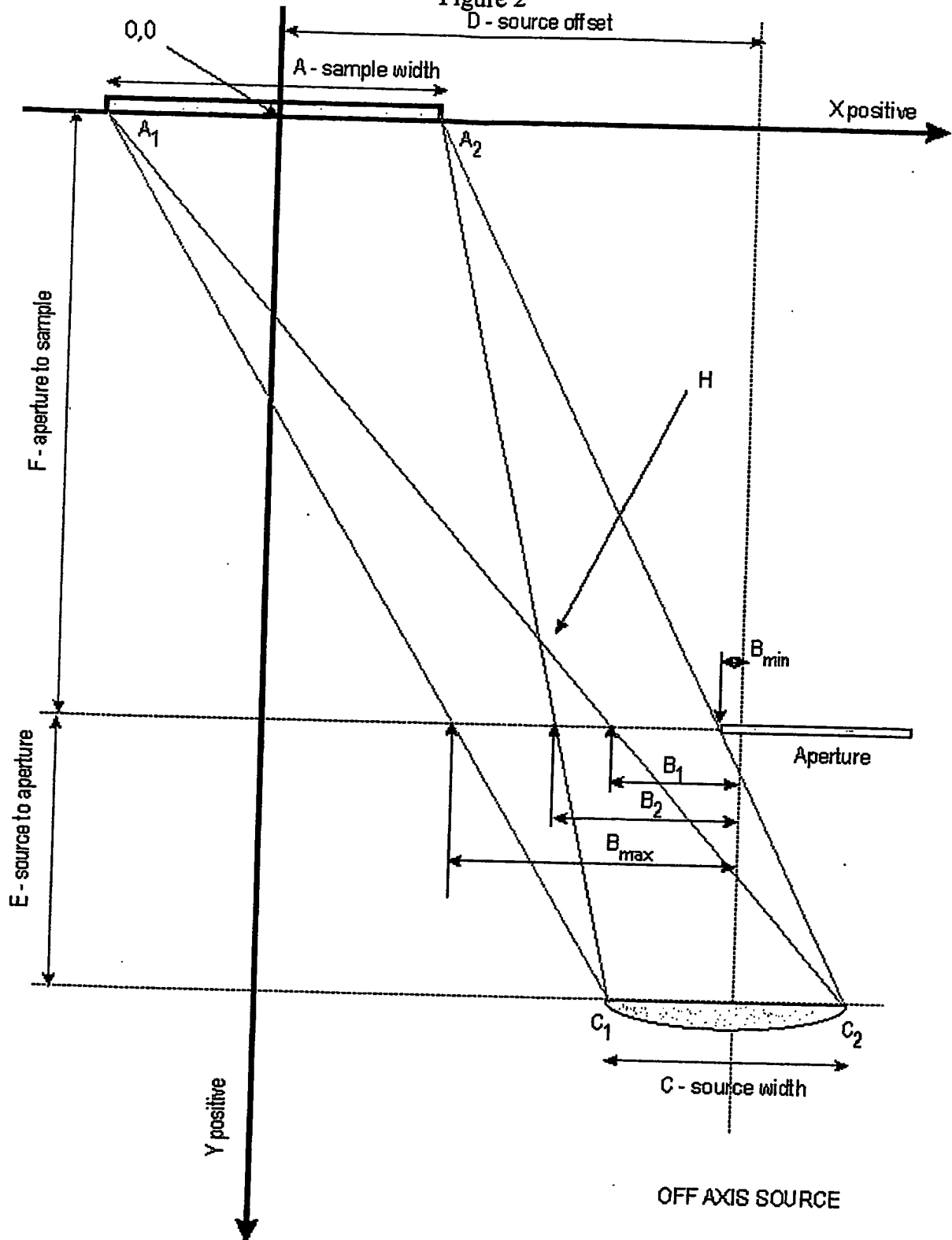
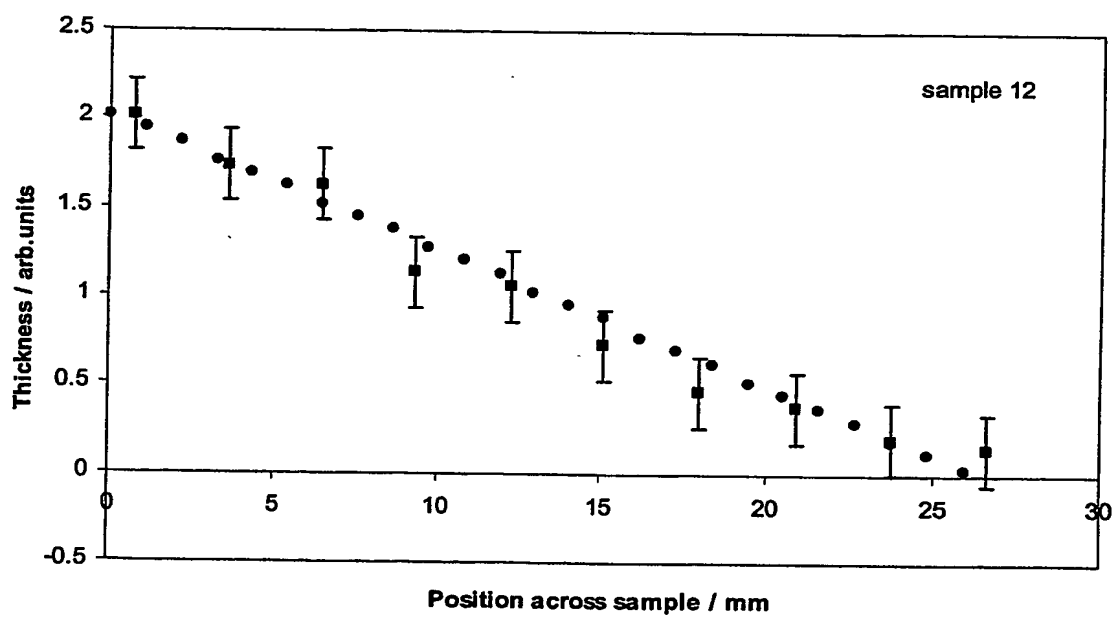
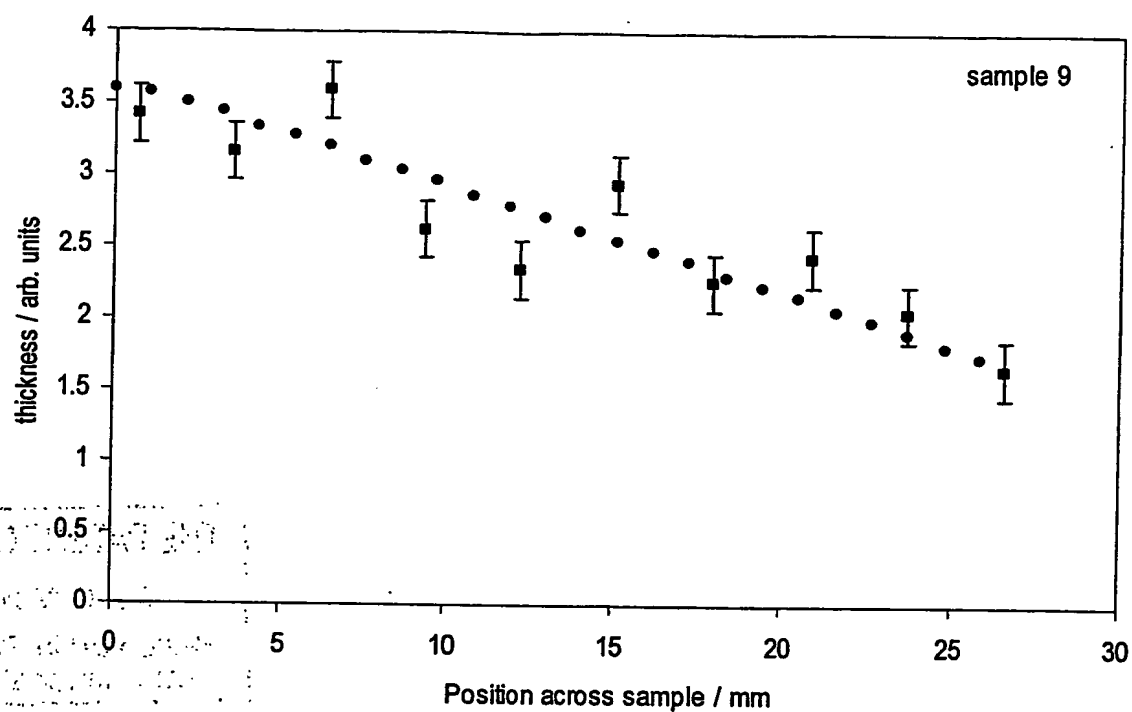




Figure 3



---

THE PATENT OFFICE

25 NOV 2004

Received in Patents  
International Unit

~~PCT/GB2004/004255~~



BEST AVAILABLE COPY